Self-grown Metal chalcogenide nanostructures for Energy storage and Electrocatalysis applications

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Submitted

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1. Introduction

Supercapacitors or electrochemical double layer capacitor (EDLC) or ultracapacitors, are energy storage devices that endow high energy density and power density compared to conventional capacitors and batteries. Increase in demand for vehicles and portable electronic devices in various applications leading a great motivation to researchers and academicians for exploring numerous energy storage systems with high energy and power density [1-5]. One of the greatest challenges the current researcher facing is to develop a low-cost and environmentally friendly high power energy resources [6-11]. Supercapacitors are important electrochemical energy storage technologies for storing energy through prompt charge/discharge process, high power density and stable cycling behavior [12, 13]. They can easily fill out the space presented between redox chemical battery and traditional capacitors. Secondly, hydrogen is a promising option for clean energy, which can be produced by splitting water either in an electrocatalyzer or by photocatalysis. Electrochemical water splitting involves the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) at cathode and anode electrode materials, respectively.

1.1 Applications of nanostructures

1.1.1 Electrochemical Supercapacitor

In the twenty-first century, energy is the most essential aspects to the human lives. Energy production and consumption, a function of combustion of fossil fuel, is going to disturb the world economy. Hence, there has been increasing demand for high- performance, environmentally friendly and cost-effective renewable energy storage devices [14, 15]. Electrochemical supercapacitor (ESs) reveal high-power density, longer cycle life than batteries and higher energy density than conventional capacitors. These advantages have made them potential options for digital cameras, electric vehicles, industrial equipment and other storage devices. Also because of rapid growth of portable electronic devices market such as laptops, notebooks, mobile-phones, computers, drones and their development trend of being small, lightweight and flexible etc., have brought about and ever-rising and urgent demand for eco-friendly electrochemical energy storage and conversion systems that are lying between capacitor and batteries [16]. In future, ESs will be a significant model in technology due acceptance of energy storage systems. ESs can be good alternative to batteries which offer maximum power density, stable and long discharge time [17]. Therefore, supercapacitor (SC), also to be widely used in many field such as energy manage systems, superionic conductors, electronic power systems

and other applications. A electrochemical supercapacitor an energy storage device, which can act as a gap bridging function between batteries and conventional capacitors [18]. ES is an electrochemical device which stores the charge on electrode with high capacitance and has anode and cathode as negative terminal and working electrode, respectively, by means of electrolyte and separator in between them and is also referred as ultra/hybrid capacitor together with EDLC. The electrolyte may be in the form of solid, liquid and gel. As compared to rechargeable batteries, the charge-discharge processes of supercapacitor are much faster. Supercapacitors are divided into symmetric and asymmetric on the basis of their configuration in which energy storage depends on the accumulation of charge or reversible redox reactions [19, 20]. Over the ordinary batteries and fuel cells, ESs have the advantage of long discharging time, easy operating, and high temperature range [21]. The hybrid ESs are the devices that have high capacitance and energy storage capabilities and combined properties of EDLC and pseudocapacitors, i.e., combination of EDLC and pseudocapacitor [22-24]. Due to rapid repeatable redox reactions among electroactive units lying on active electrode materials and an electrolyte solution in pseudocapacitor, there is storage of energy in device which generally occurs in metal oxides, metal chalcogenides and polymer based materials [25]. EDLC is the electrical storage system of carbon based structures electrostatic charging of the electrical double-layer formed at the electrode-electrolyte interface and there for termed as electrical double-layer capacitor.

Therefore, depending on the charge storage mechanism and research and development trends, electrochemical capacitors are classified into three types, namely;

(a) Electrochemical double layer capacitor (EDLC)
(b) Pseudocapacitor (PC) and
(c) Hybrid capacitors

- **Literature review**

Now a day's transition metal chalcogenide with high conductivity have been widely researched for the application of supercapacitors, rechargeable lithiumion batteries and dye-sensitized solar cells because of their outstanding performance. Recently, research activities focused on developing electrode material based on abundant, economic and ecofriendly metal sulfides and metal selenide with different morphologies, such as Co_3S_4, NiS, MnS, Bi_2S, CuS, NiSe, CuSe etc,. along with oxides, carbides and hydroxides because the cost of RuO_2 and platinum electrode material are on niche place of electronic market [26-28]. Among the family of metal sulfide,

nickel sulfide has attracted much interest because it contains number of phases including α-NiS, β-NiS, NiS_2, Ni_3S_2, Ni_3S_4, Ni_7S_6, Ni_9S_8 etc. [29]. Consequently, Ni has been reported to form very stable NiSe, $NiSe_2$ and Ni_3Se_2 phases under ambient conditions. For pseudocapacitance electrode materials, the electrochemical properties of Ni_3S_4, Ni_3S_2, NiS, NiO and NiSe are being studied widely because of their high capacitance, long using life, economical efficiency and low toxicity [30].

The 3-D Ni-foam (NiF) gives enough micro-cavities for easy percolation of electrolyte ions. Among such Ni based nanostructures Shinde et al. reported the hydrothermally synthesized self-grown Ni_xS_y superstructures for electrochemical supercapacitor with the areal specific capacitance of 7152 $F.cm^{-2}$ at current density of 1 $mA.cm^{-2}$ for the Ni_xS_y-STS electrode [31]. Krishnamoorthy *et al.* successfully synthesized Ni_3S_2 using thiourea as a sulfur source to obtain sulfide nickel foam with specific capacitance of 1293 F g^{-1} at current density of 5 $mA.cm^{-2}$ [32]. Yang *et al* fabricated mashroom-like Ni_3S_2/Ni electrode through dissolution-precipitation process by using thioacetamide as a sulfur source to corrode the nickel foam that exhibited 1190.4 F g^{-1} significant specific capacitance of at current density of 8 A g^{-1}[33].

Notably, in all cases discussed above comprising cost-effective self-developed metal chalcogenide nanostructures consisting of various morphologies, series resistances, high surface areas, in addition to in-depth chemical synthesis mechanism for electrochemical energy storage application.

1.1.2 Electrocatalysis

The water splitting process for oxygen and hydrogen production by an electrochemical processes is a simple approach to producing cleaner energy compared to the current fossil fuel generation methods for example, Among the known catalysts, Heterojunction-based composite nanostructured electrode materials have demonstrated an excellent chemical and mechanical stability and porosity, high surface area, fine controlled pore coordination, i.e., pore-size distribution and connectivity, good conductivity, low cost, and stability. Hydrogen is a promising option for clean energy, which can be produced by splitting water either in an electrocatalyzer or by photocatalysis. The oxygen evolution reactions (OERs) is multi-step four-electron process, and two electron process of hydrogen evolution reactions (HERs) are typically employed in batteries, supercapacitors, fuel cells for storing and conversion of electrochemical energy. The production of hydrogen, oxygen, or both from the electrolysis of water is a promising option to making full use of clean, earth abundant, pollution-free renewable energy. Thus far, platinum

and ruthenium-based compounds are being commonly used as noble catalytic metals for water splitting processes, the most significant electrode materials for water spitting reactions include nickel, and its composite compounds. In particular, nickel-based nanostructures like NiS, Ni_3S_2, NieNi_3S_2, NiSe, Ni_3Se_2, etc., are being utilized for water splitting applications due to their outstanding catalytic activity, excellent electrical conductivity, cost-effective synthesis processes, and eco-friendly nature for both OERs, and HERs, respectively.

1.2 Methodology

In ESs, compact nanostructures that are directly grown porous nanostructured electrodes have more importance because of their high surface area and sufficient availability of active surface sites for faradaic redox reactions and with different morphologies on either nickel-foam, copper, titanium etc. To obtain the electroctrode materials for the ES various physical and chemical methods such as electrodeposition, chemical bath deposition, successive ionic layer adsorption and reaction, sol-gel etc., are being used. In all such methods generates either film or powder products. Herein, in the present work nickel-foam will be used as skeleton for obtaining various nanostructures as it has following advantages;

a) The collection of generated charge is easy because of the low interfacial resistance,
b) high surface area of the product, and
c) the charge transfer resistance between the electrode/electrolyte interface is smaller.

The Ni-foam not only acts as 3D support but also serves as nickel-ion source. Due this there is the enhancement of electrical contact and strong mechanical adherence for fast and stable redox reaction with high ion diffusivity. Because of the environmental friendliness, cost-effectiveness, abundancy the nickel-based hydroxide, oxide, and chalcogenide electrode materials are most favorable. Ni-Foam itself contributes some SC performance to self-grown electrode materials, thus gives improved overall electrochemical performance. The most convenient method for self-grown synthesis of electrode material is the hydrothermal method.

1.2.1 Hydrothermal Method

In hydrothermal synthesis method there is the synthesis of electrode materials in various nanostructures on conducting and non-conducting substrate surfaces at temperature of less than

200 ºC and ambient pressure. In this process, there is the teflon-lined stainless-steel autoclave which posses the base current collector in the presence of suitable solvent at an annealing temperature less than 200º C for a few h. There is the production of the material on the host metallic substrate as a by-product, and this is because of reaction bath pressure and temperature. Therefore, this self-grown synthesis method provides following benefits

a) a good lattice match between the base conductive material and the product material,

b) production of different morphologies with different surface areas, which increases the overall redox reaction rate and thus electrochemical performance.

c) fast and easy charge transportation.

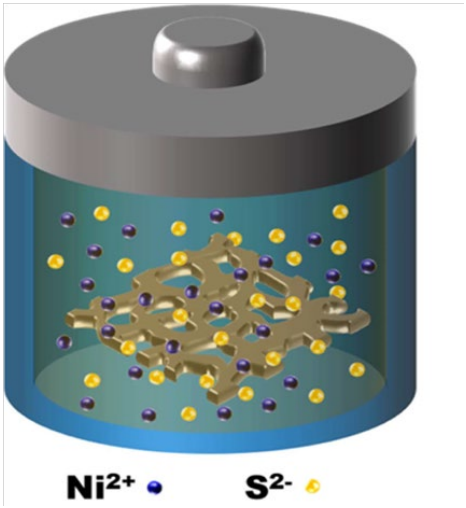

Figure 1. Schematic of hydrothermal process used for *in-situ* growth of Ni-based chalocogenides/hydroxides/oxides.

1.2.1.1 Self-grown metal chalcogenide nanomaterials

The self-grown metal chalcogenide materials and there composites will be synthesized using hydrothermal synthesis method. The as-prepared metal chalcogenide nanomaterials will be employed to their electrochemical supercapacitor measurements and electrocatalysis measurements.

1.2.1.2 Morphology-dependent metal chalcogenide nanostructures

The transition metal chalcogenide nanomaterials will be synthesized using self-grown synthesis method for different morphologies. Such metal chalcogenide materials will be synthesized at different temperatures, different deposition time durations, different precursor solutions. The as-prepared metal chalcogenide materials will be employed for their structural, morphological and electrochemical supercapacitor measurements and will also be used for electrocatalytic application.

1.2.1.3 P_H dependent nanostructures

The precursor solution to be used in hydrothermal synthesis method will be differing in P_H value so as to study the change in morphology and phases in the metal chalcogenide nanomaterials. The P_H-based supercapacitor endowed demonstrate a high capacity capacitor with a capacitance value much higher than other capacitors, but with lower voltage limits, that bridges the gap between electrolytic capacitors and rechargeable batteries [5]. The transition metal chalcogenide nanomaterials will be synthesized using autoclave-mediated self-grown synthesis method under different P_H conditions what will be envisaged for the application of electrocatalysis and supercapacitor

1.2 Characterizations

A concise account of the instruments and techniques used for acknowledgement of structural, morphological, electrical and electrochemical supercapacitor properties of the self-grown electrode materials.

1.3.1 Structural analysis

X-ray diffraction) technique is a one of the influential, renowned and most appropriate techniques for structural revelation of materials prepared in the form of films or powders.

1.3.2 Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique used to observe vibration, rotational, and other low-frequency modes in a system.

1.3.3 Fourier transform infrared spectroscopy

FT-IR spectroscopy is a tool for investigation of the various chemical groups present in the sample material.

1.3.4 Morphology monitoring

Field-emission scanning electron microscopy will be used for investigating the surface morphology of the as-prepared composite electrodes.

1.3.5 High resolution transmission electron microscopy

HR-TEM, one of most powerful techniques is used in the characterization of nanostructuress. It has capacity to inspect the constitutional characteristics of nanocomposites such as grain shape and size, crystallinity and chemical variations at a nanometer scale resolution.

1.3.6 Electrochemical workstation

The as-prepared chalcogenide composite nanostructures will be used to prepare electrodes for supercapacitor and electrocatalysis applications. The IVIUM electrochemical workstation will be used to measure Cyclic-Voltammetry (CV), Galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS). Also, Mott-Schottky measurements will be carried out for confirmation the type of conductivity and also for knowing the flat band potential of the composite nanostructured electrodes.

1.4 Objectives

This thesis aims at achieving the following objectives;

1. to develop and synthesize novel materials like metal-chalcogenides, metal-chalcogenide composites and transition metal-doped metal chalcogenides for supercapacitor and electrochemical catalytic applications.
2. To see the effect of electrolyte solutions on growth morphology followed energy storage performance.
3. To obtained the better electrocalytic activity of respective electrode materials for development of active low cost electrocatalyst for OER and HER activity.
4. To report obtained results in high indexed journals

1.5 Plausible outcomes

- Synthesis of metal chalcogenide nanostructures with their composite nanostructures and to study their physical and chemical properties.
- Fabrication of metal chalcogenide nanostructure and composite nanostructure-based electrochemical supercapacitor devices with high energy and power density followed moderate chemical stability.
- Fabrication of meatal chalcogenide nanostructures and composites as a potential electrocatalyst for OER and HER activities.
- Writing and publishing research articles, reviews and patents.

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